

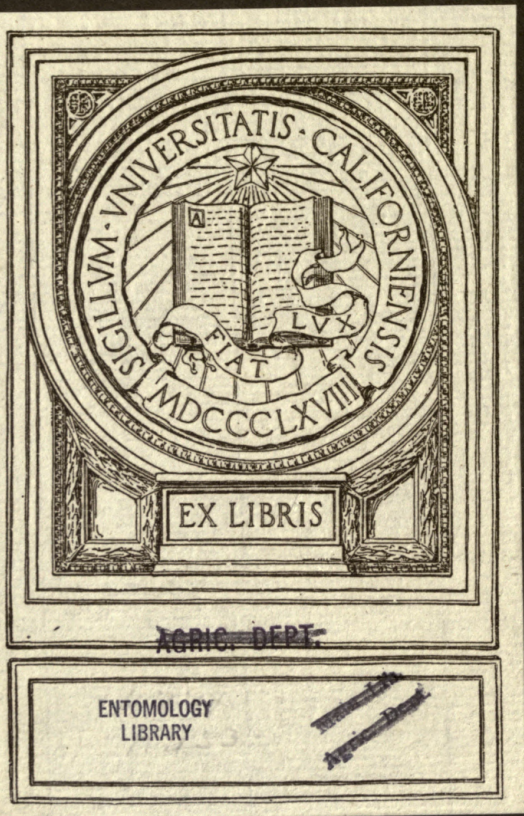
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Some Chemical Relations of
Lime-Sulphur Solutions,
Lead Arsenate and Nicotine
C.C. Hedges

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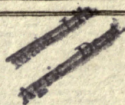


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Some Chemical Relations of Lime-
Sulphur Solutions, Lead Arsenate
and Nicotine

A
THESIS

PRESENTED TO THE FACULTY OF THE
GRADUATE SCHOOL
OF
CORNELL UNIVERSITY

FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

BY
CHARLES CLEVELAND HEDGES

1912

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INTRODUCTION

The introduction of lime-sulphur spray compound into New York State about the year of 1907 and 1908 caused a great many inquiries as to their variation, and value of it as a repression of blister-mite and San Jose scale. However, apparently slight changes in material used or in methods, have resulted in compounds widely different in appearance; spraying qualities, and insecticidal value or effect. The uncertainty of securing the best results with the home made mixtures, due to their variation, and the unpleasant features connected with the making of it at home caused many to welcome the advent of the commercial preparations in concentrated form. The number of brands grew very rapidly due to the marked success of the first, when in 1909 there were at least five on the market. The comparison of the different strengths of the several brands, led to the investigation as to their comparative value.

So with the advent and marked success of the Lime-sulphur preparation, as a spraying material, for the control of the blister-mite and San Jose scale the question of combining materials as the Arsenate of Lead and Nicotine preparations, naturally came to be considered essential, as a saver of time and expense.

At the suggestion of Professor Cavanaugh, of the Chemistry Department, and Professor Crosby, of the Entomological Department, a chemical study of the reactions with reference to the advisability of mixing Lime-sulphur solution, Lead Arsenate, and Nicotine preparations together for the control of San Jose scale, Red Bugs, etc., by one spraying, was begun, with the results as given in this paper.

HISTORICAL

CHEMICAL BASIS OF LIME-SULPHUR PREPARATIONS

The insecticidal value of these lime-sulphur washes rests, not in any mechanical mixture of the two but to the chemical compounds formed by the union of lime or rather calcium and sulphur. In what particular manner the lime sulphur solution acts as an insecticide and fungicide, no one has yet clearly demonstrated. What specific compounds are directly responsible for the effects produced we are not yet certain. If we mix together the two elements in a dry form namely, calcium in the form of lime (CaO) and sulphur they would not combine and would have no effect on each other, but when brought together in a boiling water solution for about forty-five minutes to one hour, they combine to not only form one compound but a series of compounds called calcium polysulphides (CaS_x).

At least two of these compounds are very soluble in water and are very destructive to insect life with which they are brought in contact. There may be formed at least five compounds of calcium and sulphur; since one part of calcium may combine with four-fifths its weight of sulphur, or with two-three, four or five times that amount. The different calcium sulphides in the

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lime-sulphur are not very readily separable; so the exact insecticidal value of each has not been carefully determined but it has been generally assumed that the two highest sulphides are the most efficient; and of these two the one higher in sulphur, the pentasulphide (CaS_5) is supposed to be of a higher insecticidal value. In freshly prepared solutions only two of these compounds are present, the four sulphur compound or calcium tetrasulphide (CaS_4) and the five sulphur compound or calcium pentasulphide (CaS_5). Calcium pentasulphide contains 20 per cent of calcium and 80 per cent of sulphur, which is at the rate of four parts of sulphur by weight for one part of calcium. Calcium tetrasulphide contains 24 per cent of calcium and 76 per cent of sulphur, which is at the rate of 3.2 parts of sulphur by weight for one part of calcium. Calcium tetrasulphide and pentasulphide produce the orange-red color in the solution. In the chemical changes that take place between lime and sulphur when they are heated in water, another compound is unavoidably formed, but in smaller amounts; this is a chemical compound of three elements calcium, sulphur and oxygen. This calcium thiosulphate (CaS_2O_3) which is easily soluble in water and is therefore contained in the solution along with the sulphides of calcium. The value of this compound for spraying purposes is not known but on exposure to air it is changed by oxidation to calcium sulphite (CaSO_3) and free sulphur. Calcium sulphite is insoluble in water and therefore appears in the sediment or in the undissolved portion of lime-sulphur preparations, usually forming the chief part of the sediment. The free sulphur formed by the decomposition of thio-sulphate recombines with calcium and goes into solution in the operation of making lime-sulphur solution, when enough lime is present. The sulphite may later take up more oxygen and form calcium sulphate (CaSO_4) an insoluble part of the sediment. The desirable chemical changes are the formation of the soluble lime-sulphur combinations, the calcium tetrasulphide and the calcium pentasulphide and perhaps the formation of the calcium thio-sulphate; the indersirable reactions are the oxidizing of the thio-sulphate, after the mixture cools, with the formation of sulphates and sulphites (1).

EFFICIENCY OF LIME-SULPHUR IN RELATION TO CHEMICAL COMPOSITION

Dr. L. L. VanSlyke in Bulletin No. 329, of the New York State Experiment Station at Geneva, states "that it is held, as the results of some experimental work that the effect of the lime sulphur mixture is not due to the direct action of calcium penta-sulphide (CaS_5) or calcium tetra-sulphide (CaS_4) but is due rather to compounds that are formed from those, either calcium thio-sulphate (CaS_2O_3) or free sulphur or both.

If the direct effective substance is calcium thiosulphate, then the amount that can be formed from the lime-sulphur solution is directly dependent upon and proportional to the amount of calcium pentasulphide or calcium tetrasulphide in solution.

(1) Bul. No.319 and No. 320 New York Experiment Station (Geneva)

Of the sulphur set free from the pentasulphide, tetrasulphide and thio-sulphate is the effective agent, then the amount of compounds in solution capable of furnishing the largest amount of free sulphur directly determines the value of the solution. Calcium pentasulphide is capable of furnishing more free sulphur by decomposition than the tetrasulphide and this more than the thiosulphate.

If the free sulphur is the material desired then the solution containing the largest amount of pentasulphide is the most valuable. It is now commonly believed, whether correct or not, that the solution containing the most pentasulphide is the most effective, at least in connection with the destruction of scale insects. What ever may prove to be the facts in relation to the manner of action of the lime-sulphur solution, it is obvious that its efficiency stands close and direct relation to the amount of sulphide compounds contained in it, or, in other words, to the chemical composition of the solution."

The difference in concentration and amount of Calcium thio-sulphate (CaS_2O_3) present in home-made solutions, compared with the more concentrated form prepared by manufacturers are caused by the manufacture in preparing a more concentrated solution, by evaporation, changes some of the calcium thio-sulphate to calcium sulphite leaving a smaller percentage of calcium thiosulphite in solution than in the home-made preparations. The calcium sulphite, as formed under the conditions stated is found in the sediment as such or oxidized to Calcium sulphate (CaSO_4) which is insoluble and in either form is a loss to the manufacturer, and the consumers.

ARSENATE OF LEAD

This substance was first prepared as an insecticide by Mr. F. C. Moulton in 1892, while acting as chemist in Malden, under Mr. E. H. Forbush, Field Director, in charge of the work of destroying the gypsy moth.

In the work of destroying the gypsy moth it was soon discovered that Paris green would not kill many of the caterpillars, even when used in as large a proportion in water as was possible without injury to the foliage of the trees. It therefore seemed necessary, to discover, if possible, some insecticide that would destroy the caterpillar and at the same time not injure the most delicate foliage.

The first public mention of arsenate of lead was in the report of the Massachusetts Agricultural College, October, 1893, page 23.

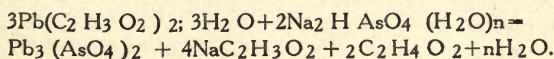
The name "gypsino" was given to this insecticide by Mr. Moulton, but as there was an entirely different product on the market by the same name, this insecticide was called arsenate of lead.

CHEMICAL COMPOSITION

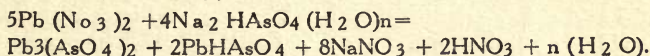
The arsenate of lead used in spraying, operations, to be exact, is not a salt whose composition may be expressed by a single formula, but instead is a mixture of both diplumbic and tri-plumbic arsenates, the relative quantities of each depending principally upon the source of the soluble lead salt used in making it.

In the preparation of the arsenate of lead it is only necessary to form a chemical union between the common lead oxide (litharge), PbO , and arsenic pentoxide, (As_2O_5) , but in order to obtain a product suitable for use as an insecticide, the chemical union must take place between soluble salts containing these oxides. In general practice, arsenate of lead suitable for spraying purposes is prepared by bringing together commercial grades of acetate or nitrate of lead and arsenate of soda. Owing to the variable composition of these commercial salts, a chemical analysis is indispensable, as indicating the relative amounts to be used. All such calculations must be based on the quantity of lead oxide (PbO) found in the lead salt and that of arsenic pentoxide (As_2O_5) contained in the arsenate of soda, making due allowance for the other acidulous radicals which may precipitate the lead.

Where the acetate of lead is used approximately the whole of the arsenate of lead product consists of tri-plumbic arsenate, as indicated in the following equation.



The following equation represents the reaction between arsenate of soda and nitrate of lead by Smith:--(1)



EFFICIENCY AS A SPRAYING MATERIAL.

Arsenate of lead remains in suspension in water much longer than Paris green, because of its very low specific gravity, which is 1.00688 while that of Paris green is 3.42225. In spraying, the low specific gravity of arsenate of lead and its consequent suspension in water for a considerable length of time make it possible to distribute it more evenly over vegetation. The white color is also a decided advantage, for one is enabled to see at a glance whether a tree or shrub has been sprayed; and it is a noteworthy fact that this insecticide adheres to foliage for longer than any similar substance now in use. It is undoubtedly true that larger proportions of arsenate of lead must be used than of Paris green but this can be done with entire safety to the vegetation. The cost of the insecticide forms a very small part of the cost of spraying; and since arsenate of lead remains on the foliage so much longer than other insecticides, a much larger proportion can be used and even then be much cheaper than substances which wash off readily in showers, making it necessary to spray the trees the second time.

A large percentage of the spraying at the present time is with a mixture of an insecticide and a fungicide; because as has already been said, the great expense is in the labor, and not in the materials used; and when the insecticide and fungicide can be applied together, the cost of one spraying is saved. Ar-

(1) Annual Report State Board of Agriculture, 1897, page 354.

senate of lead can be mixed with Bordeaux mixture, very successfully, just the same as Paris green.

The investigation concerning the mixing Lime-sulphur with Arsenate of Lead was published by C. E. Bradley and H. V. Tartar (1) with the following results in connection with further studies of the reaction of Lime-sulphur solution and alkali waters on Lead Arsenate. Haedden has stated (2) that Lead Arsenate is more soluble in water containing alkali salts than in mineral waters.

TABLE I.

Composition of the Lime-sulphur Solution before and after addition of Lead Arsenate.

	Blank Lime-sulphur	Grams per 1000cc. Filtrate from acid arsenate and Lime-sulphur	Filtrate from neut- ral Arsenate Lime-sulphur
Total Sulphur	10.750	10.256
" CaO	4.380	4.060
" As ₂ O ₅		.095	.012

Above results indicate that 8 times as much arsenate is rendered soluble from the acid arsenate as from the neutral, or calculated from original material this would be equivalent to 0.25 percent. of soluble As₂ O₅ from neutral 1.98 percent. As₂ O₅ from acid Lead Arsenate. Distinct losses of sulphur and lime have also taken place in the acid arsenate mixture and it is evident that there is a mutual decomposition when acid lead arsonate is mixed with the lime sulphur solution.

TABLE II.

Analysis of the residue from the Mixture of Lime-Sulphur and Lead Arsenate.

	Neutral Lead Arsenate residue Percent.	Acid Lead Arsenate residue Percent.
Free Sulphur	0.70	20.80
PbS	1.47	14.80
CaO		10.40

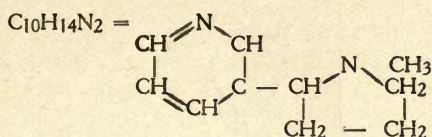
The reactions and loss of sulphur and lime from solution, as shown above are much more pronounced with the acid than with neutral arsenate and it is therefore advisable to employ the neutral form when desiring to combine lime-sulphur and lead arsenate. Waters containing considerable quantities of alkali carbonates should be avoided in mixing lead arsenate for spraying purposer, as their tendency is to render the arsenic soluble and do not dissolve the lead. Soluble arsenic is one of the most important things to avoid as in most cases it is the main cause for the injury to foliage.

(1) Journal Industrial Engineering Chemistry, Vol. II, No. 7, p. 328, (1910)

(2) Bulletin 131 Colorado Experiment Station.

NICOTINE.

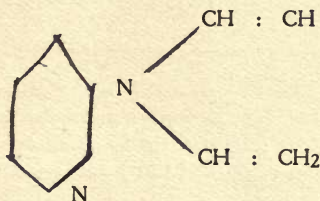
Nicotine- α -Pyridyl- β -tetrahydro-n-methyl pyrrol (?)



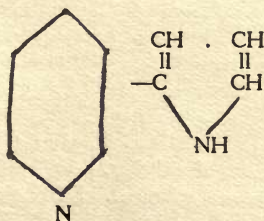
boiling at 247° , with Specific gravity 1.011 (15°), and Laevocrotatory occurs in the leaves of the tobacco plant, *Nicotiana Tabacum*, in quantities varying from 0.6 to 8 per cent, depending upon the varieties. As a rule, the better qualities of tobacco contain less nicotine than the poorer sorts.

HISTORY.

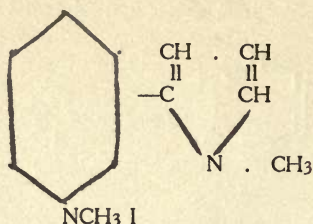
Posselt and Remian discovered nicotine (1828). Since 1991 Blau, but more especiallo Pinner, has studied its transposition reactions, the constitutional formula proposed by Pinner harmonizes with its deportment and has more recently been forfeited by the experiments of Ame Pictet and Cropioux (1895), which doubtless led to the synthesis of nicotine by Pictet (C. R. 1903, 137, 810) and has been shown to be pyridyl-N-methyl-pyrrolidine. The method of synthesis is as follows:- Nicotine acid is transformed first into its ethylester, and then into the amide; this bromine and alkali (Hoffman's reaction) gives amino-pyridine and when the salt of this base with mucic acid is distilled, N-pyridyl-pyrrole.



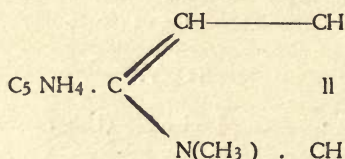
is formed. When the vapour of this compound is passed through a heated tube, it is transformed into the isomeric α -pyridyl-pyrrole,



This forms a potassic derivative which with methyliodide yields



and this, when distilled with lime, gives



α -pyridyl-N-methyl pyrrol, which can be converted into α -pyridyl-N-methyl pyrrolidine (i-nicotine) by the addition of hydrogen. The racemic alkaloid thus obtained may be resolved into its optically active components by the aid of α -tartaric acid when, γ -nicotine-d-tartrate crystallizes out first.

OCCURENCE

In leaves of tobacco (*Nicotiana Tabacum*) and in the leaves of *Macrophylla rustica* and *N. glutinosa*. Occurs also in Pituri. According to Zeise and Vohl and Eulenberg it is not present in tobacco smoke, but Heubel obtained evidence of its presence therein.

PREPARATION

Tobacco leaves (10 parts) are soaked in water 24 hours, and the mixture heated to 100° by steam. The aqueous extract is mixed with lime (1 part) and distilled. The distillate is neutralized by oxalic acid and evaporated to a thin syrup. Addition of concentrated KOH now separates the base, which is rectified in a current of hydrogen.

PROPERTIES

Colorless liquid, not frozen at -10°. Smells like tobacco, unless it is quite pure. It is very hygroscopic. Mixes with water, developing heat, and is very soluble. It has a disagreeable odor and burning taste. A very violent poison. Leavorotatory. Optical activity of its aqueous solution varies greatly with concentration in a 4 percent. solution. $[d]_D = -77^\circ$ at 20°: in a .88 percent. solution $[d]_D = -79^\circ$. Solutions of salts of nicotine are dextrorotatory. Nicotine turns brown on exposure to air and light. Its solutions are strongly alkaline. Its very soluble in water, alcohol, ether, terpenes and fatty oils. At 100° it dissolves 10 percent. of sulphur, but on cooling it separates again. Ether extracts it from aqueous solutions. KOH separates it from aqueous solutions.

ESTIMATION

(1) By distilling with potash, extracting the distillation with ether, evaporating the ether, converting the residue into sulphate and repeating the process. (2) Tobacco is mixed with aqueous NaOH and some alcohol, and extracted with ether. The extract is evaporated and the nicotine distilled over with steam and estimated by titration with standard acid, or by the polarimeter.

EXPERIMENTAL.

OUTLINE OF EXPERIMENTS.

1. Determination of Total Sulphur and Lime (CaO) in a dilute Lime-sulphur solution of the different strengths as used in the experiments.

2. Determination of the amount of Nicotine, sulphur trioxide, (SO_3) and the acidity or alkalinity of the different Nicotine preparations used, as Nicotine sulphate, Black Leaf 40, and Nico-fume.

3. Determination of the soluble Arsenic oxide (As_2O_5) and the acidity of the arsenate of Lead used.

4. Mixing of the Lime-sulphur of the different dilutions with the arsenate of Lead at the rate of four pounds of the Lead arsenate to one hundred gallons of the solution, and determining the amount of total sulphur and Lime (CaO) remaining in solution. Also filtering, drying, and weighing sediment. Using both acid and neutral Lead Arsenate.

5. Mixing the solutions as in number four and trying the effect of carbon dioxide (CO_2), as in the carbon dioxide spraying apparatus, on the increase of the soluble Arsenic Oxide (As_2O_5) and the solution and the decrease of the efficiency of the mixture.

6. Mixing the solutions of the Lime-sulphur and arsenate lead, again, as in number four and adding 2 cc of the different Nicotine preparations to the mixture and making to a definite volume (1000 cc). Then determining the amount of Total Sulphur and Lime (CaO) remaining in solution. Also filtering, drying, and weighing the sediment.

7. Effect of carbon-dioxide (CO_2) as in spraying apparatus upon a dilute Nicotine solution, diluting one to four hundred.

8. Preparation of Nicotine Sulphate from tobacco stems or poor grade tobacco.

METHODS OF ANALYSIS

DETERMINATION OF NICOTINE

Solutions required are (a) Alcoholic soda.-Dissolve 6 grams of sodium hydroxide in 40 cc. of water and 60 cc of 90 per cent. alcohol. (b) Sodium hydroxide.-Dissolve 4 grams of sodium hydroxide in 1000 cc of water. (c) Sulphuric Acid.-A standard solution.

Weigh out from 5 to 6 grams of tobacco extract into a small beaker. Add 10 cc of the alcoholic soda solution and follow with enough chemically pure powdered calcium carbonate to form a moist but not a lumpy mass. Mix the

whole thoroughly and transfer to a Soxhlet extractor and exhaust for about five hours with ether. Evaporate the ether solution at a low temperature by holding over the steam bath, and take up the residue with 50 cc of the dilute sodium hydroxide solution. Transfer this residue by means of water to a 500 cc Kjeldahl flask, and distill in a current of steam, using a condenser. (Use a few pieces of pumice, and a small piece of paraffin, to prevent bumping and frothing.) Continue the distillation till all the nicotine has passed over the distillate usually varying from 400 to 500 cc. When the distillation is complete, only about 15 cc. of the liquid should remain in the distillation flask. Titrate the distillate with standard sulphuric acid using cochineal as indicator. One molecule of sulphuric acid solution is equivalent to two molecules of nicotine. This is the Official method adopted by the Official Agricultural Chemists.

DETERMINATION OF TOTAL SULPHUR

Take an aliquot portion of the solution representing 1 to 2 cc of the original concentrated Lime-Sulphur solution, place in a 200 cc. beaker, with 25 cc. of hydrogen peroxide (H_2O_2), 2 cc of concentrated Sodium hydroxide and about 25 cc of water. Then the beaker after being covered with a beaker cover was placed on the water bath for two hours until all of the sulphur was oxidized to calcium sulphate. After oxidation is complete, neutralize the solution with hydrochloric acid, precipitate the sulphur with Barium Chloride solution as Barium Sulphate. Let stand over night, filter and weigh the precipitate after ignition, in a platinum or porcelain crucible.

DETERMINATION OF LIME (CaO)

Take an aliquot portion of the dilute Lime-sulphur solution and oxidize the sulphur in the solution with hydrogen peroxide, as in the determination of Total Sulphur; make the solution acid with acetic acid, then alkaline with ammonium hydroxide and precipitate the calcium as calcium oxalate. Filter the solution while hot, wash precipitate thoroughly and place the filter paper containing the precipitate in hot water containing about 5 cc of concentrated sulphuric acid. Titrate the solution with a standard Potassium permanganate solution in the usual manner.

The determination of Total Arsenic and water soluble arsenic was determined by the methods outlined in the Bulletin No. 107 (revised) of the Official Agricultural Chemists, Department of Agriculture, Bureau of Chemistry, solution used in the experiment:-

1. Concentrated Lime-sulphur solution.

Specific Gravity = 1.1750 or 21° Baume'.

Per cent Total Sulphur = 12.86

Per cent Total Lime (CaO) = 6.43

Per cent Calcium (Ca) = 4.59

2. Nicotine solution called Black Leaf 40, Nicotine sulphate or Nico-sul.

Specific Gravity of solution at 15° C. = 1.2120.

Per cent of Nicotine in the solution = 40.50

Per cent of combined Nicotine (as sulphate) = 13.12

Acidity expressed as H_2SO_4 = 12.13 percent.

Came the same using Phenolphthalein or Cochineal as Indicator.

Total Sulphur in 2 cc of solution \equiv .1274 grams or 5.25 percent
Sulphur in solution as $H_2 SO_4$ in 2 cc \equiv .0960 grams or 3.96 percent

Sulphur in solution combined to Nicotine \equiv .0314 grams or 1.29 percent

Trace of Lime in the solution.

Some of the Nicotine in the solution is not combined as sulphate although there was an excess of $H_2 SO_4$ present. The Nicotine may be combined in some way with the organic matter present. Quite a little organic matter is present in this solution.

3. Nicotine solution called Nico-fume.

Specific Gravity of the solution at $15^\circ C.$ \equiv 1.0139

Per cent of Nicotine in solution \equiv 36.04

Per cent of Nicotine combined as sulphate \equiv 6.15

Total sulphur in 2 cc, of solution \equiv .0123 grams or .60 per cent.

Sulphur in solution combined to Nicotine \equiv .0123 grams.

There is no lime present in the solution.

Solution is Alkaline.

Alkalinity (Phenolphthalein as ind.) expressed as $NaOH$ \equiv .24 p. ct.

Alkalinity (Cochinical as Indicator) expressed as $NaOH$ \equiv 1.01 percent

The increased alkalinity with cochinical as indicator may be due entirely to free Nicotine present. Solution does not contain hardly any organic matter, and is not very thick.

4. Nicotine solution called Rextract, which is a mixture of Nicotine and Lime-sulphur containing some sediment.

Hydrogen sulphide is given off of the solution abundantly.

Total sulphur in 2 cc. of the solution \equiv .2822 grams.

Total Lime (CaO) in 2 cc. of the solution \equiv .1841 "

Total Calcium in 2 cc. of the solution \equiv .1315 grams

Hard to obtain a uniform sample of the solution and sediment

5. Grasselli's Arsenate of Lead-Paste, and Hemingway's Lead Arsenate

Both of these were acid.

(Grasselli's) Acidity expressed as $H_2 SO_4$ \equiv 0.31 percent.

(Hemingway's) " " " " \equiv 0.37 percent.

6. Solution of Hydrogen Peroxide.

Total Sulphur in 50 cc. of the solution \equiv .0040 grams.

Total Lime (CaO) in 50 cc. of the solution \equiv none

Experiment No. 1 was to determine the amount of sulphur and Calcium lost from the Lime-sulphur solution by mixing 2 cc of the Nicotine compound with a dilute Lime-sulphur of the dilution 1:10.

TABLE A.

100 cc of the Lime-sulphur solution was diluted to 1000 cc by the addition of water after the following were added:

Per 100cc of Solution	Dilute Lime sulphur Sol.	2cc Nico-fume	2cc Nico-sul (acid)	2cc Nico-sul (neut)	2cc Rextract
Grams of Sediment	trace	trace	trace	trace	trace
Grams of Total S.	2.0090	1.8778	1.8153	1.8583	1.7878
Grams of S. lost	0.0000	0.1312	0.1937	0.1507	0.2212
Grams of Lime	0.7492	0.7485	0.7473	0.7490	0.7476
Grams of Lime lost	0.0000	0.0007	0.0019	0.0002	0.0016
Grams of Calcium	0.5351	0.5346	0.5338	0.5350	0.5340
Grams of Ca. lost	0.0000	0.0005	0.0013	0.0001	0.0011
Percent loss of Total S.	none	6.53	9.64	7.50	11.01
Percent loss of Calcium	none	0.09	0.24	0.00	0.20

The result in experiment number one, as found in the Table, A shows that at the dilution of one to ten a very small percentage of calcium is thrown out of solution by mixing any of the Nicotine compounds with Lime-sulphur solution and the acid Nicotine thrown out almost three times as much calcium out of solution as the Nico-fume which is alkaline, and twenty four times as much as with the neutral "Nico-sul" compound. The loss of calcium in any of the mixtures are not large and hardly to be considered. As to the sulphur there is more than three percent more of sulphur thrown out of the solution by the use of acid "Nico-sul" compound than with the alkaline solution of Nico-fume and a little more than two percent more sulphur is lost by the use of acid "Nico-sul," compound than with the neutral "Nico-sul" solution. The alkaline "Nico-fume" solution throws out of solution more calcium than the neutral "Nico-sul" solution due to the alkaline substance replacing some of the lime. With the sulphur lost it is just the opposite as the lime-sulphur solution is alkaline and the alkaline "Nico-fume" helps to hold it in solution. At this dilution the results show that it is best to use neutral or slightly alkaline Nicotine and not the acid Nicotine solutions, as acid "Nico-sul" compounds with the lime-sulphur solutions. The use of Rextract is not advisable as it is a mixture of Lime-sulphur solution and Nicotine compound and contains a large quantity of hydrogen sulphide, besides the difficulty of obtaining a uniform

sample due to large quantity of sediment present in the preparation.

Experiment No. 2 was to determine the amount of sulphur and Calcium lost from the Lime-sulphur solution by the mixing of 2 cc. of the Nicotine solution with a dilute Lime-sulphur solution of the dilution 1:20.

TABLE B

50 cc. of the concentrated Lime-sulphur solution was diluted to 1000 cc. by the addition of water after the following was added.-

Per 100cc of Solution	Dilute Lime- sulphur Sol.	2cc Nico- fume	2cc Nico- sul (acid)	2cc Nico- sul (neut)	2cc Rextract
Grams of Sediment	trace	trace	0.0290	trace	trace
Grams of Total S.	.8332	.8040	0.7929	.7857	.8166
Grams of S. Lost	.0000	.0292	0.0403	.0475	.0166
Grams of Lime	.3760	.3716	0.3752	.3760	.3746
Grams of Lime lost	.0000	.0044	0.0008	.0000	.0014
Grams of Calcium	.2686	.2654	0.2680	.2686	.2677
Grams of Ca. lost	.0000	.0032	0.0006	.0000	.0009
Percsnt loss of Total S	.0000	3.50	4.83	5.70	1.99
Percent loss of Calcium	.0000	1.19	.22	.00	.33

The results in Experiment number two found in Table B. shows that at the dilution of one to twenty a very small quantity of Calcium is thrown out of solution by the mixing, just the same as in number one. The "Nico-fume" which is alkaline throws out of solution 1.19 percent of Calcium due to the replacement of the Lime by the alkaline substance, while the neutral "Nico-sul" solution causes no loss of Calcium and the loss due to the acid Nico-sul solution was .22 of one percent. showing, that the acid Nico-Sul in the more dilute solution had not as detrimental effect. As to the sulphur there were 1.33 percent more sulphur thrown out of solution by the acid Nico-sul solution than with the alkaline Nico-fume solution showing approximately the same results as shown at the dilution of one to ten. In the more dilute solution of one to twenty there was proportionally more sulphur deposited by the neutral Nico-sul than in the dilution of one to ten, and .87 of one per cent more sulphur thrown out by the use of neutral Nico-sul than with the acid Nico-sul. At the dilution of one to twenty the results indicate that it is best to use neutral or just slightly alkaline Nicotine compounds and not the acid Nicotine solution, as "Nico-Sul," with the dilute Lime-sulphur solution.

Although the use of neutral Nico-sul solution gave a slight higher result in the loss of sulphur than the acid Nico-sul solution, the loss of Calcium was not as great.

TABLE E.

25 cc. of the concentrated Lime-sulphur solution was diluted to 1000 cc. by the addition of water after the following were added:

Per 100 cc. of Sol.	Dilute Lime-sul- Solution	Lead Ar- senate (acid)	2cc. Nico- sul. (acid) Lead Arse- nate (acid)	2cc. Nico- sul. (neut.) Lead Arse- nate (neut)	2cc. Nico- fume (alka) Lead Arse- nate (acid)
Grams of Total S.	.3708	.3072	.2693	.3565	.3468
Grams of S. lost	.0000	.0636	.1015	.1043	.0240
Grams of Lime	.1836	.1800	.1768	.1720	.1772
Grams of Lime lost	.0000	.0036	.0068	.0116	.0064
Grams of Calcium	.1311	.1285	.1263	.1228	.1266
Grams of Ca. lost	.0000	.0026	.0048	.0083	.0045
Percent. loss of Total S.	.0000	17.15	27.37	3.08	6.47
Percent. loss of Calcium.	.0000	1.98	0.36	6.32	3.43

The results in Experiment No. 5, as found in Table E. shows that at the dilution of one to forty the largest loss of sulphur was when the 2 cc. of acid Nico-sul and the acid Lead Arsenate were used together giving a loss of 27.37 percent of sulphur and a loss of only .36 of one percent of Calcium. The acid Lead Arsenate gave a loss of 17.15 percent of sulphur and 1.98 percent of Calcium, showing that the Lead Arsenate mixed with 2 cc. of acid Nico-sul has a stronger reaction on a solution of Lime-sulphur diluted one to forty than on a dilution of one to twenty than the Lead Arsenate alone, this also shows that an acid solution of Nicosul throws out of solution more sulphur from a solution of one to forty dilution than a one to twenty dilution as also indicated in Experiment three. where the dilute Lime-sulphur was treated alone with 2 cc. of acid Nico-sul. The amount of Calcium lost is very small in all of the mixtures, showing that an excess of alkali has a tendency to throw it out of solution as shown when alkaline Nico-fume is used.

At the dilution of one to forty the results indicate that it is best to use as near neutral solution of Nicotine compound that is obtainable and a neutral Lead Arsenate when mixing them with a dilute Lime-sulphur solution.

Experiment No. 6, was to determine the amount of Sulphur and Calcium lost from the Lime-sulphur solution by the addition of exactly neutral or slightly alkaline Lead Arsenate at the rate of four pounds to 100 gallons of the solution containing 2 cc. of neutral or slightly alkaline Nicotine compound. Dilution of the Lime-sulphur solution was one to forty.

TABLE F.

25 cc. of the concentrated Lime-sulphur solution was diluted to 1000 cc. by the addition of water after the following were added:-

Per 100 cc. of Sol.	Dilute Lime-sul. Solution	Exactly Neutral Lead Ar- senate	Exactly Neutral Lead Ar- senate Nico-fume	Slightly Alkaline Lead Ar- senate Nico-sul	Slightly Alkaline Lead Ar- senate Nico-fume
Grams of Total S.	.3708	.3656	.3648	.3468	.3432
Grams of S. lost	.0000	.0052	.0060	.0240	.0276
Grams of Lime	.1836	.1824	.1755	.1504	.1504
Grams of Lime lost	.0000	.0012	.0080	.0332	.0332
Grams of Calcium	.1311	.1303	.1254	.1074	.1074
Grams of Ca. lost	.0000	.0008	.0057	.0237	.0237
Percent. loss of Sulphur	.0000	1.40	1.62	6.47	7.44
Percent. loss of Calcium	.0000	0.65	5.41	18.08	18.08

The results in Experiment No. 6, as found in Table F. shows that at the dilution of one to forty the largest loss of sulphur was when the slightly alkaline Lead Arsenate and the alkaline Nico-fume were used; and when the slightly alkaline Lead Arsenate and Nico-sul solution were used, showing that it is just as bad to have an alkaline solution as an acid solution, because the alkaline replaces the lime due to it being stronger base, and the lime forms the sediment with some of the sulphur that was combined with the Calcium forming the Calcium pentasulphide (CaS_5) which is very unstable. As the other results show, to have the best results a neutral solution of a Nicotine compound and an exactly neutral Lead Arsenate should be used with the dilute Lime-sulphur solution for the control of the San Jose scale, Red Bugs, etc. with one spraying. There may be some slight variations in results but the most of them support this conclusion.

In some experimental work performed by Mr. Wallace of the Department of Plant Pathology, it was observed that some lime-sulphur solutions diluted one to thirty and saturated with carbon dioxide before being applied to the trees was effective for certain troubles and caused no leaf injury. When, however, there was added to the Lime-sulphur solution lead arsenate, at the rate of four pounds to one hundred gallons, there was caused some black precipitate, and the mixture then precipitated with carbon dioxide there was considerable leaf injury. Some trees were nearly completely defoliated. The lead arsenate of the same brand as used above, when sprayed alone with water caused slight injury. Lead arsenate mixed with Lime-sulphur solution as above, but without any connection of carbon dioxide showed a slight injury, but only after a period of about one month.

The investigation of the problem as given was taken up with the following conclusions:-

The injury caused by the Lead Arsenate alone, when sprayed, was due to the soluble arsenic (As_2O_5) which was .36 of one percent and it can be increased by passing Carbon-dioxide into the solution.

When Lime-sulphur solution is treated with Lead Arsenate some Lead sulphide is formed, the black precipitate, and Calcium arsenate setting free some sulphur and hydrogen sulphide. The retarded injury caused by the mixing of lead arsenate with lime-sulphur wash was due to the calcium of the lime sulphur uniting with some of the soluble arsenic of the Lead Arsenate when they were mixed. Then by the action of the carbon dioxide of the air upon the calcium in combination, the arsenic (As_2O_5) was made soluble after a period of almost a month.

The Lime-sulphur solution when saturated with carbon-dioxide and then sprayed gives no injury, but when the lime-sulphur solution is first treated with lead-arsenate then saturated with carbon dioxide, it gives considerable leaf injury caused by the action of the carbon-dioxide on the lime-sulphur solution forming calcium carbonate and some hydrogen sulphide. The hydrogen sulphide reacts with the lead arsenate forming lead sulphide (the black precipitate) and some soluble arsenic, which does the injury. Lead Sulphide is precipitated from water containing Lead Arsenate by passing hydrogen sulphide into it, although lead arsenate is insoluble in water.

Lead arsenate used had .36 of one per cent of soluble Arsenic (As_2O_5), when dissolved in distilled water; but when treated with water, which had been saturated with Carbon-dioxide, it had .44 of one percent of soluble arsenic (As_2O_5) showing that water containing carbon-dioxide, as hard waters, have a greater dissolving power on Lead Arsenate. Therefore in making up spraying solutions should use as soft a water as obtainable. The Lead Arsenate and Lime-sulphur solution after being saturated with carbon-dioxide has .66 of one per cent of soluble arsenic (As_2O_5) showing that the carbon-dioxide pressure sprayers cannot be used with a mixture of Lime-sulphur and lead arsenate, although it can be used to advantage with the Lime-sulphur solution alone as the decomposition is very small and the free sulphur being in such a fine condition would act as a fungicide which fact has been demonstrated. Some soluble arsenic may also be produced by the action of the carbon-dioxide on the calcium arsenate formed by the action of Lime-sulphur solution on the lead arsenate. The soluble arsenic is the damaging product to the foliage so it is advisable to have the arsenic in as insoluble form as possible. It is advisable, to avoid injury to foliage, in the use of any arsenical spraying material, that may contain some free or soluble arsenic, to use some milk of lime in excess, that is Calcium hydroxide solution, so as to take care of any soluble arsenic present. This can also be used with the mixture of Lime-sulphur and lead arsenate, especially when the Lead arsenate, which is to be mixed with the dilute Lime-sulphur solution, is slightly acid. This treatment of the Lead Arsenate before mixing with the dilute Lime-sulphur solution would certainly be advisable, especially as a preventative of injury to foliage.

SUMMARY

1. There is no reaction between dilute Lime-sulphur solution and dilute Nicotine solution.

2. In the use of Nicotine compounds with dilute Lime-sulphur solution, the best dilution of Lime-sulphur solution to use is one to forty.

3. The use of acid Nicotine Compounds, as "Nico-sul" is not advisable with dilute Lime-sulphur solution, because a sediment is produced composed mostly of free sulphur, which decreases its value as an insecticide or fungicide to that amount.

4. If a too alkaline Nicotine Compound is used a sediment composed principally of Lime (CaO) and a small amount of free sulphur is produced.

5. To obtain the best results it is advisable to use an exactly neutral or as near neutral Nicotine Compound as is obtainable; such as "Nico-fume", with dilute Lime-sulphur solutions. In which case only a trace of sediment is formed.

6. Acid Lead Arsenate cannot be used with dilute Lime-sulphur solutions.

7. Neutral Lead Arsenate is the best to use with dilute Lime-sulphur solution, and also to use with dilute Lime-sulphur and Nicotine Compounds for the control of San Jose scale, Red Bugs, etc, with one spraying.

8. As soft a water, as is obtainable, should be used in making up Lead Arsenate for spraying because waters high in dissolved salts, or in carbon dioxide, makes proportionately more arsenic (As_2O_5) soluble.

9. Carbon Dioxide pressure sprayers cannot be used in the spraying of Lead Arsenate, or when Lead Arsenate and dilute Lime-sulphur solution are mixed, as more soluble arsenic (As_2O_5) is dissolved.

10. To avoid soluble Arsenic in Lead Arsenate and to neutralize the acidity of the Lead Arsenate in its use with the Lime-sulphur solution, use an excess of milk of Lime with the mixture. It can also be used to neutralize the acidity of Nicotine Compounds.

11. Carbon Dioxide pressure sprayers can be used safely with the dilute Nicotine preparations.

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